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Field dependence of the temperature at the peak of the zero-field-cooled magnetization

H Kachkachi†¶, W T Coffey‡, D S F Crothers§, A Ezzir†, E C Kennedy§, M Noguès† and E Tronc‖

† Laboratoire de Magnétisme et d'Optique, CNRS, Université de Versailles St Quentin, 45, avenue des Etats-Unis, 78035 Versailles Cédex, France
‡ Department of Electronics and Electrical Engineering, Trinity College, Dublin 2, Ireland
§ Department of Applied Mathematics and Theoretical Physics, The Queen's University of Belfast, Belfast BT7 1NN, UK
‖ LCMC, CNRS, Université Pierre et Marie Curie, 75252 Paris Cédex 05, France

E-mail: kachkach@physique.uvsq.fr

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Abstract. The effect of an applied magnetic field on the temperature at the maximum of the zero-field-cooled (ZFC) magnetization, M_{ZFC}, is studied using the recently obtained analytic results of Coffey *et al* (Coffey W T *et al* 1998 *Phys. Rev. Lett.* **80** 5655) for the prefactor of the Néel relaxation time which allow one to precisely calculate the prefactor in the Néel–Brown model and thus the blocking temperature as a function of the coefficients of the Taylor series expansion of the magnetocrystalline anisotropy. The present calculations indicate that even a precise determination of the prefactor in the Néel–Brown theory, which always predicts a monotonic decrease of the relaxation time with increasing field, is insufficient to explain the effect of an applied magnetic field on the temperature at the maximum of the ZFC magnetization. On the other hand, we find that the non-linear field dependence of the magnetization along with the magnetocrystalline anisotropy appears to be of crucial importance to the existence of this maximum.

1. Introduction

Experimental results obtained a few years ago for ferrofluids [1] and recently for γ-Fe_2O_3 nanoparticles [2] indicate that for dilute samples (weak interparticle interactions), the temperature $T_{\max}$ at the maximum of the zero-field-cooled magnetization, M_{ZFC}, first increases with increasing field, attains a maximum and then decreases. More recently, additional experiments performed on γ-Fe_2O_3 particles dispersed in a polymer [3] confirmed the previous result for dilute samples and showed that, in contrast, for concentrated samples (strong interparticle interactions), $T_{\max}$ is a monotonically decreasing function of the magnetic field [3] (see figure 1).

The behaviour observed for dilute samples (isolated nanoparticles) is rather unusual since one intuitively expects the applied field to lower the energy barrier and thus the blocking temperature of all particles and thereby the temperature ${T_{\max}}^+$. Resonant tunnelling is one of the suggestions which have been advanced [4] for the mechanism responsible for the

¶ Author to whom any correspondence should be addressed.
+ The temperature $T_{\max}$ at the maximum of the ZFC magnetization is assumed to be roughly given by the average of the blocking temperatures T_B of all particles in the (dilute) assembly.

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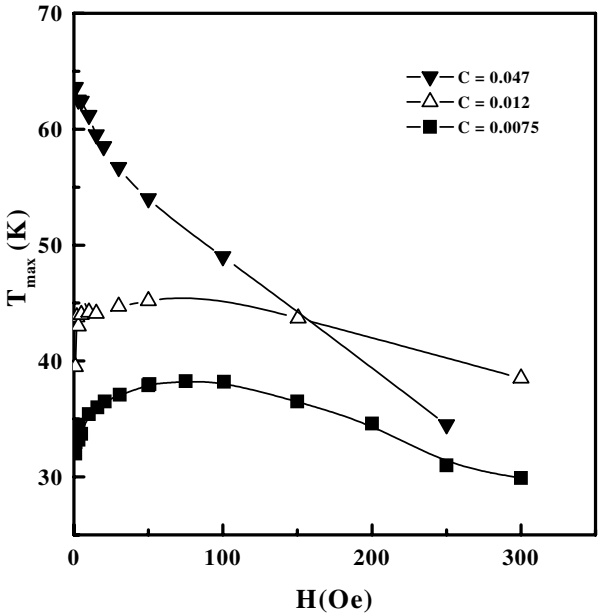


Figure 1. The temperature $T_{\max}$ at the maximum of the ZFC magnetization plotted against the applied field for different sample concentrations. The volume fraction of the particles in the sample 4D (γ-Fe_2O_3, mean diameter $\sim$8.32 nm) determined from the density measurements is $C_v = 0.0075, 0.012, 0.047$.

increase of the relaxation rate around zero field. More recently, M_{ZFC}-measurements [2] have shown an anomaly in the temperature range 40–60 K, which is probably too high for quantum effects to manifest themselves. Yet another explanation [2] of the $T_{\max}$-effect was proposed using arguments based on the particle anisotropy barrier distribution. It was suggested that for randomly oriented particles of a *uniform size*, and for small values of the field, the field depresses the energy barriers, and thereby enlarges the barrier distribution, so lowering the blocking temperature. It was also suggested that the increase of the barrier-distribution width overcompensates for the decrease of the energy barrier in a single particle. However, the discussion of the relaxation time was based on the original Arrhenius approach of Néel. Here the escape rate, that is the inverse relaxation time, is modelled as an attempt frequency multiplied by the Boltzmann factor of the barrier height, with the inverse of the attempt frequency being of the order of 10^{-10} s, thus precluding any discussion of the effect of the applied field and the damping parameter on the prefactor, and so their influence on the blocking temperature.

It is the purpose of this paper to calculate the blocking temperature using the Kramers theory of the escape of particles over potential barriers as adapted to magnetic relaxation by Brown [5]. The advantage of using this theory is that it allows one to precisely calculate the prefactor as a function of the applied field and the damping parameter (provided that interactions between particles are neglected). Thus the behaviour of the blocking temperature as a function of these parameters may be determined. It appears from the results that even such a precise calculation is unable to explain the maximum in the blocking temperature T_B as a function of the applied field. Thus an explanation of this effect is not possible using the Néel–Brown model for a *single* particle, as that model invariably predicts a monotonic decrease of T_B as a function of the applied field.

In view of this null result we demonstrate that the T_{max}-effect may be explained by considering an assembly of non-interacting particles having a volume distribution. This is accomplished by using Gittleman's [6] model which consists of writing the zero-field-cooled magnetization of the assembly as a sum of two contributions, one from the blocked magnetic moments and the other from the superparamagnetic ones, with the crucial assumption that the superparamagnetic contribution is given by a non-linear function (the Langevin function) of the applied magnetic field and temperature. If this is done, even the simple Néel–Brown expression for the relaxation time leads to a maximum in T_{max} for a wide range of values of the anisotropy constant K. It was claimed in [7] that a simple volume distribution, together with a Néel expression for the relaxation time, leads to the same result for FeC particles, although the author used the Langevin function for the superparamagnetic contribution to the magnetization.

Therefore, the particular expression for the single-particle relaxation time which is used appears not to be of crucial importance in the context of the calculation of the blocking temperature.

In the next section we briefly review Kramers' theory of the escape rate.

2. Kramers' escape-rate theory

The simple Arrhenius calculation of reaction rates for an assembly of *mechanical particles* undergoing translational Brownian motion, in the presence of a potential barrier, was much improved upon by Kramers [8]. He showed, by using the theory of the Brownian motion, how the prefactor of the reaction rate, as a function of the damping parameter and the shape of the potential well, could be calculated from the underlying probability-density diffusion equation in phase space, which for Brownian motion is the Fokker–Planck equation (FPE). He obtained (by linearizing the FPE about the potential barrier) explicit results for the escape rate for intermediate-to-high values of the damping parameter and also for very small values of that parameter. Subsequently, a number of authors [9, 10] showed how this approach could be extended to give formulae for the reaction rate which are valid for all values of the damping parameter. These calculations have been reviewed by Hänggi *et al* [11].

The above reaction-rate calculations pertain to an assembly of mechanical particles of mass m moving along the x-axis, so the Hamiltonian of a typical particle is

$$H = \frac{p^2}{2m} + V(q) \tag{1}$$

where q and p are the position and momentum of a particle and $V(q)$ is the potential in which the assembly of particles resides; the interaction of an individual particle with its surroundings is then modelled by the Langevin equation

$$\dot{p} + \varsigma p + \frac{\mathrm{d}V}{\mathrm{d}q} = \lambda(t) \tag{2}$$

where $\lambda(t)$ is the Gaussian white noise and ς is the viscous drag coefficient arising from the surroundings of the particle.

The Kramers theory was first adapted to the thermal rotational motion of the magnetic moment (where the Hamiltonian, unlike that of equation (1), is effectively the Gibbs free energy) by Brown [5] in order to improve upon Néel's concept of the superparamagnetic relaxation process (which implicitly assumes discrete orientations of the magnetic moment and which does not take into account the gyromagnetic nature of the system). Brown in his first explicit calculation [5] of the escape rate confined himself to axially symmetric (functions of the latitude only) potentials of the magnetocrystalline anisotropy, so the calculation of the

relaxation rate is governed (for potential-barrier height significantly greater than k_BT) by the smallest non-vanishing eigenvalue of a one-dimensional Fokker–Planck equation. Thus the rate obtained is valid for all values of the damping parameter. As a consequence of this very particular result, the analogy with the Kramers theory for mechanical particles only becomes fully apparent when an attempt is made to treat non-axially symmetric potentials of the magnetocrystalline anisotropy which are functions of both the latitude and the longitude. In this context, Brown [5] succeeded in giving a formula for the escape rate for magnetic moments of single-domain particles, in the intermediate-to-high-damping (IHD) limit, which is the analogue of the Kramers IHD formula for mechanical particles. In his second 1979 calculation [5] Brown only considered this case. Later, Klik and Gunther [12], by using the theory of first-passage times, obtained a formula for the escape rate which is the analogue of the Kramers result for very low damping. All these (asymptotic) formulae which apply to a general non-axially symmetric potential were calculated explicitly for the case of a uniform magnetic field applied at an arbitrary angle to the anisotropy axis of the particle by Geoghegan *et al* [13] and compare favourably with the exact reaction rate given by the smallest non-vanishing eigenvalue of the FPE [14–16] and with experiments on the relaxation time of single-domain particles [17].

In accordance with the objective stated in the introduction, we shall now use these formulae (as specialized to a uniform field applied at an arbitrary angle by Geoghegan *et al* [13] and Coffey *et al* [14–16]) for the calculation of the blocking temperature of a single particle.

A valuable result following from these calculations will be an explicit demonstration of the breakdown of the non-axially symmetric asymptotic formulae at very small departures from axial symmetry, manifesting itself in the form of a spurious increase in $T_{\max}$. Here interpolation formulae joining the axially symmetric and non-axially symmetric asymptotes (analogous to the one that joins the oscillatory and non-oscillatory solutions of the Schrödinger equation in the WKBJ method [18]) must be used in order to reproduce the behaviour of the exact reaction rate given by the smallest non-vanishing eigenvalue of the FPE, which always predicts a monotonic decrease of $T_{\max}$, as has been demonstrated by Garanin *et al* [19] in the case of a transverse field.

3. Calculation of the blocking temperature

Following the work of Coffey *et al* cited above, the effect of the applied magnetic field on the blocking temperature is studied by extracting T_B from the analytic (asymptotic) expressions for the relaxation time (the inverse of the Kramers escape rate) [14–16], which allow one to evaluate the prefactor as a function of the applied field and the dimensionless damping parameter η_r in the Gilbert–Landau–Lifshitz (GLL) equation. For single-domain particles the equation of motion of the unit vector describing the magnetization inside the particle is regarded as the Langevin equation of the system (detailed in [20]).

Our discussion of the Néel–Brown model as applied to the problem at hand proceeds as follows.

In an assembly of ferromagnetic particles with uniaxial anisotropy excluding dipole–dipole interactions, the ratio of the potential energy vU to the thermal energy k_BT of a particle is described by the bistable form

$$\beta U = -\alpha(\boldsymbol{e}\cdot\boldsymbol{n})^2 - \xi(\boldsymbol{e}\cdot\boldsymbol{h}) \tag{3}$$

where: $\beta = v/(k_BT)$ with v the volume of the single-domain particle; $\alpha = \beta K \gg 1$ is the anisotropy (reduced) barrier height parameter; K is the anisotropy constant; $\xi = \beta M_s H$ is the external field parameter; $\boldsymbol{e}$, $\boldsymbol{n}$ and $\boldsymbol{h}$ ($h \equiv \xi/2\alpha$) are unit vectors in the directions of

the magnetization $\boldsymbol{M}$, the easy axis, and the magnetic field $\boldsymbol{H}$, respectively. θ and ψ denote the angles between $\boldsymbol{n}$ and $\boldsymbol{e}$ and between $\boldsymbol{n}$ and $\boldsymbol{h}$, respectively. The Néel time, which is the time required for the magnetic moment to surmount the potential barrier given by (3), is asymptotically related to the smallest non-vanishing eigenvalue λ_1 (the Kramers escape rate) of the Fokker–Planck equation by means of the expression $\tau \approx 2\tau_N/\lambda_1$ [5], where the diffusion time is

$$\tau_N \simeq \frac{\beta M_s}{2\gamma}\left[\frac{1}{\eta_r} + \eta_r\right]. \tag{4}$$

γ is the gyromagnetic ratio, M_s the intrinsic magnetization, η the phenomenological damping constant and η_r the GLL damping parameter $\eta_r = \eta\gamma M_s$.

As indicated above, Brown [5] at first derived a formula for λ_1, for an arbitrary *axially symmetric* bistable potential having minima at $\theta = (0, \pi)$ separated by a maximum at θ_m, which when applied to equation (3) for $\boldsymbol{h} \parallel \boldsymbol{n}$, i.e. a magnetic field parallel to the easy axis, leads to the form given by Aharoni [21], with $\theta_m = \cos^{-1}(-h)$:

$$\lambda_1 \approx \frac{2}{\sqrt{\pi}}\alpha^{3/2}(1-h^2)\left[(1+h)\mathrm{e}^{-\alpha(1+h)^2} + (1-h)\mathrm{e}^{-\alpha(1-h)^2}\right] \tag{5}$$

where $0 \leqslant h \leqslant 1$, $h = 1$ being the critical value at which the bistable nature of the potential disappears.

In order to describe the non-axially symmetric asymptotic behaviour, let us denote by $\beta\,\Delta U_-$ the smaller reduced barrier height of those corresponding to the escape from the left or the right of a bistable potential. Then for very low damping, i.e. for $\eta_r\beta\,\Delta U_- \ll 1$ (with of course the reduced barrier height $\beta\,\Delta U_- \gg 1$, depending on the size of the nanoparticle studied), we have [5, 16, 20] the following asymptotic expression for the Néel relaxation time:

$$\tau_{VLD}^{-1} \approx \frac{\lambda}{2\tau_N} \approx \frac{\eta_r}{2\pi}\left\{\omega_1\beta(U_0-U_1)\mathrm{e}^{-\beta(U_0-U_1)} + \omega_2\beta(U_0-U_2)\mathrm{e}^{-\beta(U_0-U_2)}\right\} \tag{6}$$

For the intermediate-to-high damping, where $\eta_r\beta\,\Delta U_- > 1$ (again with the reduced barrier height $\beta\,\Delta U_-$ much greater than unity), we have [16] the asymptotic expression

$$\tau_{IHD}^{-1} \approx \frac{\Omega_0}{2\pi\omega_0}\left\{\omega_1\mathrm{e}^{-\beta(U_0-U_1)} + \omega_2\mathrm{e}^{-\beta(U_0-U_2)}\right\} \tag{7}$$

where

$$\omega_1^2 = \frac{\gamma^2}{M_s^2}c_1^{(1)}c_2^{(1)} \qquad \omega_2^2 = \frac{\gamma^2}{M_s^2}c_1^{(2)}c_2^{(2)}$$

$$\omega_0^2 = -\frac{\gamma^2}{M_s^2}c_1^{(0)}c_2^{(0)}$$

$$\Omega_0 = \frac{\eta_r g'}{2}\left[-c_1^{(0)} - c_2^{(0)} + \sqrt{(c_2^{(0)} - c_1^{(0)})^2 - \frac{4}{\eta_r^2}c_1^{(0)}c_2^{(0)}}\right]$$

$$g' = \frac{\gamma}{(1+\eta_r^2)M_s}.$$

Here ω_1, ω_2 and ω_0 are respectively the well and saddle angular frequencies associated with the bistable potential, Ω_0 is the damped saddle angular frequency and the $c_j^{(i)}$ are the coefficients of the truncated (at the second order in the direction cosines) Taylor series expansion of the crystalline anisotropy and external field potential at the wells of the bistable potential denoted by 1 and 2 and at the saddle point denoted by 0. A full discussion of the application of these general formulae to the particular potential, which involves the numerical solution of a quartic

equation in order to determine the $c_j^{(i)}$ with the exception of the particular field angles $\psi = \pi/4$ and $\pi/2$, in equation (3) is given in references [13, 22].

The blocking temperature T_B is defined as the temperature at which $\tau = \tau_m$, τ_m being the measuring time. Therefore, using equations (4), (5) and (6) (or (4), (5) and (7)) and solving the equation $\tau = \tau_m$ for the blocking temperature T_B, we obtain the variation of T_B as a function of the applied field, for an arbitrary angle ψ between the easy axis and the applied magnetic field.

In particular, for very small values of ψ we have used equation (5), as the problem then becomes almost axially symmetric and the arguments leading to equations (6) and (7) fail [5, 13, 20], and appropriate connection formulae must be used so that they may attain the axially symmetric limit. We then sum over ψ, as the easy axes of the particles in the assembly are assumed to be randomly distributed. In figure 2 we have plotted the resulting T_B versus H for different values of the damping parameter η_r. We have checked that lowering (or raising) the value of the measuring time τ_m shifts the curve $T_B(H)$ only very slightly upwards (or downwards) while leaving the qualitative behaviour unaltered.

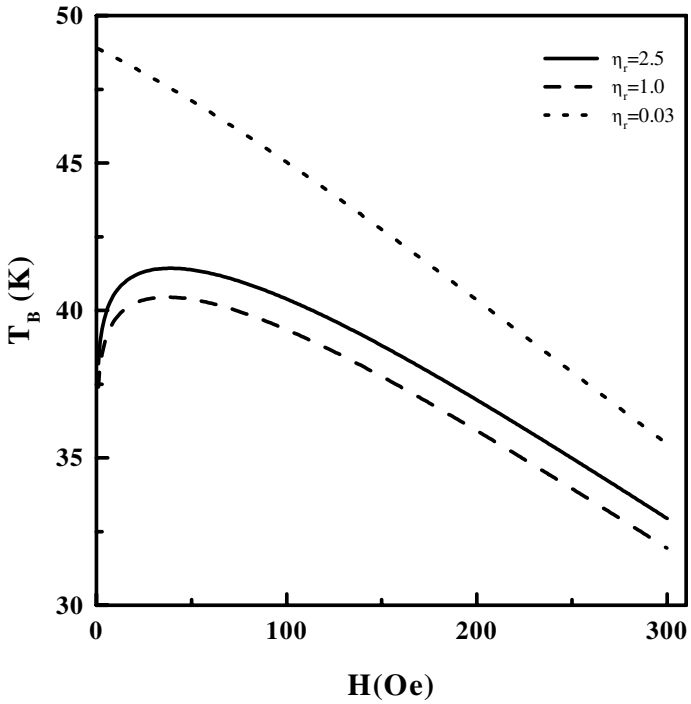


Figure 2. The blocking temperature T_B as a function of the applied field as extracted from the formulae for the relaxation time of a single-domain particle and summed over the arbitrary angle ψ, plotted for different values of the damping parameter η_r (see the text), and the mean volume $\langle V \rangle = 265$ nm^3. ($K = 1.25 \times 10^5$ erg cm^{-3}, $\gamma = 2 \times 10^7$ S^{-1} G^{-1}, $M_s = 300$ emu cm^{-3}, $\tau_m = 100$ s.)

In order to compare our analytical results with those from experiments on particle assemblies, we have calculated the temperature $T_{\max}$ at the maximum of the ZFC magnetization. In the present calculations we have assumed that M_s is independent of temperature. We find that the temperature $T_{\max}$ behaves in the same way as was observed experimentally [2, 3] for dilute samples (see figure 3, where the parameters are those of the most dilute sample in figure 1, with $\eta_r = 2.5$).

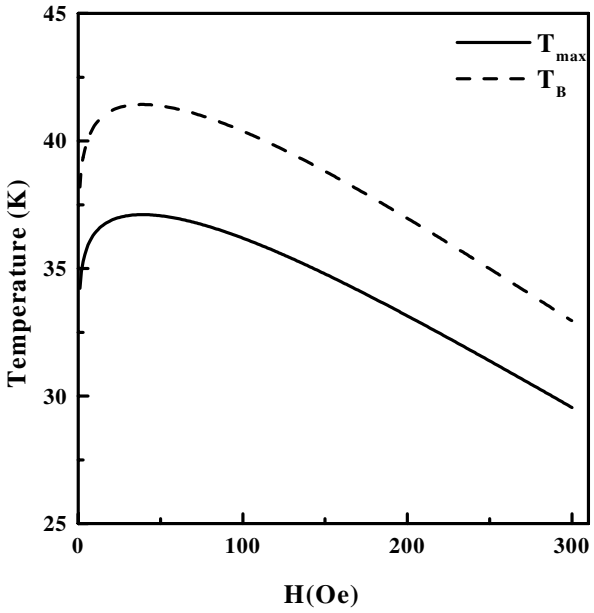


Figure 3. The temperature $T_{\max}$ at the maximum of the ZFC magnetization for an assembly of particles with randomly distributed easy axes, as a function of the applied field obtained by averaging the blocking temperature in figure 2 over the volume log–normal distribution ($\sigma = 0.85$)—see the text; with $\eta_r = 2.5$.

Moreover, our calculations for a single particle show that the blocking temperature $T_B(H)$ exhibits a bell-like shape in the case of intermediate-to-high damping. This behaviour is however spurious as is shown below.

4. Spurious behaviour of the blocking temperature at low fields

We have mentioned that initially the non-axially symmetric asymptotic formulae appear to provide the low-field behaviour of $T_{\max}$. However, this apparent behaviour is spurious as the asymptotic formulae (as one may verify (i) by exact calculation of the smallest non-vanishing eigenvalue of the Fokker–Planck equation and (ii) since e.g. the IHD formula does not continue to the axially symmetric asymptote) fail at low fields, since the IHD formula diverges like $h^{-1/2}$, for all angles, where h is the reduced field as defined in section 3. The effect of the divergence is thus to produce a spurious maximum in $T_{\max}$ as a function of the applied field.

In order to verify this, we have also performed such calculations [13, 14, 22] using exact numerical diagonalization of the Fokker–Planck matrix. The smallest non-vanishing eigenvalue λ_1 thus obtained leads to a blocking temperature which agrees with that provided by the asymptotic formulae with the all-important exception of the case for IHD at very low fields where the exact calculation invariably predicts a monotonic decrease in the blocking temperature rather than the peak predicted by the IHD formula (7), so indicating that the theoretical peak is an artefact of the asymptotic expansion, caused by using equation (7) in a region beyond its range of validity—that is, in a region where the potential is almost axially symmetric due to the smallness of the applied field which gives rise to a spurious discontinuity between the axially symmetric and non-axially symmetric asymptotic formulae.

An explanation of this behaviour follows (see also [19]): in the non-axially symmetric IHD asymptote given by equation (7), which is formulated in terms of the Kramers escape rate, as the field tends to zero, for high damping, the saddle angular frequency ω_0 tends to zero. Thus the saddle becomes infinitely wide and so the escape rate predicted by equation (7) diverges, leading to an apparent rise in the blocking temperature until the field reaches a value sufficiently high to allow the exponential in the Arrhenius terms to take over. When this occurs the blocking temperature decreases again in accordance with the expected behaviour. This is the field range where one would expect the non-axially symmetric asymptote to work well.

In reality, as demonstrated by the exact numerical calculations of the smallest non-vanishing eigenvalue of the Fokker–Planck matrix, the small-field behaviour is not as predicted by the asymptotic behaviour of equation (7) (it is rather given by the axially symmetric asymptote) because the saddle is limited in size to ω_0. Thus the true escape rate cannot diverge, and the apparent discontinuity between the axially symmetric and non-axially symmetric results is spurious, leading to an apparent rise in T_B. In reality, the prefactor in equation (7) can never overcome the exponential decrease embodied in the Arrhenius factor. Garanin [23] (see [19]) has discovered bridging formulae which provide continuity between the axially symmetric equation (5) and non-axially symmetric asymptotes leading to a monotonic decrease of the blocking temperature with the field in accordance with the numerical calculations of the lowest eigenvalue of the Fokker–Planck equation.

An illustration of this was given in reference [19] for the particular case of $\psi = \pi/2$, that is a transverse applied field. If the escape rate is written in the form

$$\tau^{-1} = \frac{\omega_1}{\pi} A \exp(-\beta\, \Delta U)$$

where ω_1 is the attempt frequency and is given by

$$\omega_1 = \frac{2K\gamma}{M_s}\sqrt{1-h^2}$$

then the factor A, as predicted by the IHD formula, behaves as $\eta_r/\sqrt{h}$ for $h \ll 1, \eta_r^2$, while for $h = 0$, A behaves as $2\pi\eta_r\sqrt{\alpha/\pi}$, which is obviously discontinuous. Hence a suitable interpolation formula is required. Such a formula (analogous to that used in the WKBJ method [18]) is obtained by multiplying the factor A of the axially symmetric result by $\mathrm{e}^{-\xi} I_0(\xi)$, where $I_0(\xi)$ is the modified Bessel function of the first kind and $\xi = 2\alpha h$ (see [19]).

This interpolation formula, as is obvious from the large- and small-ξ limits, automatically removes the undesirable $1/\sqrt{h}$ divergence of the IHD formula and establishes continuity between the axially symmetric and non-axially symmetric asymptotes for $\psi = \pi/2$, as dictated by the exact solution.

It is apparent from the discussion of this section that the Néel–Brown model for a single particle is unable to explain the maximum in $T_{\max}$, as a careful calculation of the asymptotes demonstrates that they always predict a monotonic decrease in the blocking temperature. However, this effect may be explained by considering an assembly of non-interacting particles with a (log–normal) volume distribution and using Gittleman's [6] model as shown below, where the superparamagnetic contribution to the magnetization is taken to be a non-linear function (a Langevin function) of the magnetic field.

5. Possible explanation of the maximum in $T_{\max}$

Our explanation of the low-field behaviour of $T_{\max}$ is based on extracting $T_{\max}$ from the zero-field-cooled magnetization curve assuming a volume distribution of particles. According to Gittleman's model the zero-field-cooled magnetization of the assembly can be written as

a sum of two contributions, one from the blocked magnetic moments and the other from the superparamagnetic ones. In addition, we write the superparamagnetic contribution as a Langevin function of the applied magnetic field and temperature.

Gittleman *et al* [6] proposed a model in which the alternative susceptibility of an assembly of non-interacting particles, with a volume distribution and randomly distributed easy axes, can be written as

$$\chi(T,\omega) = \frac{1}{Z}\int_0^\infty \mathrm{d}V\ Vf(V)\chi_V(T,\omega) \tag{8}$$

where $Z = \int_0^\infty \mathrm{d}V\ Vf(V)$, $f(V)$ is the volume-distribution function, χ_V is the susceptibility of the volume under consideration and $\mathrm{d}V\ Vf(V)\chi_V$ is the contribution to the total susceptibility corresponding to volumes in the range V–$V + \mathrm{d}V$. χ_V is then calculated by assuming a step function for the magnetic field, i.e. $H = 0$ for $t < 0$ and $H = H_0 =$ constant for $t > 0$. Then, the contribution to the magnetization from particles of volume V is given by

$$M_V(t) = VH_0(\chi_0 - (\chi_0 - \chi_1)\mathrm{e}^{-t/\tau}) \tag{9}$$

where $\chi_0 = M_s^2(T)V/3k_BT$ is the susceptibility at thermodynamic equilibrium and $\chi_1 = M_s^2(T)V/3E_B$ is the initial susceptibility of particles in the blocked state (see [24] and many references therein). The Fourier transform of (9) leads to the complex susceptibility

$$\chi = \frac{(\chi_0 + \mathrm{i}\omega\tau\chi_1)}{1 + \mathrm{i}\omega\tau} \tag{10}$$

whose real part reads [6]

$$\chi' = \frac{\chi_0 + \omega^2\tau^2\chi_1}{1 + \omega^2\tau^2} \tag{11}$$

where τ_m is the measuring time, and ω is the angular frequency ($=2\pi\nu$).

Starting from (11), the application of an alternating field yields:

(a) $\chi' = \chi_0$ if $\omega\tau \ll 1$. At high temperature the magnetic moments orientate themselves on a great number of occasions during the measurement time, and thus the susceptibility is the superparamagnetic susceptibility χ_0.

(b) $\chi' = \chi_1$ if $\omega\tau \gg 1$. At low temperature the energy supplied by the field is insufficient to reverse the magnetic moments during the measurement time. Here the susceptibility is the static susceptibility χ_1.

Between these two extremes there exists a maximum at the temperature $T_{\max}$. χ' can be calculated from (11) using the formula for the relaxation time τ appropriate to the anisotropy symmetry and, considering a particular volume V, one can determine the temperature $T_{\max}$.

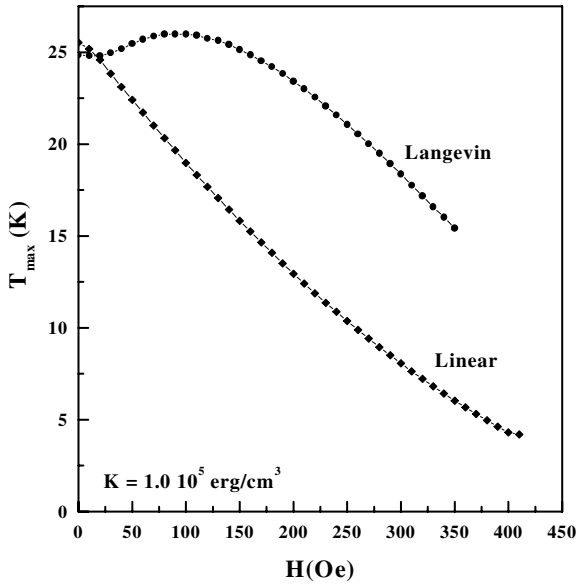
In an assembly of particles with a volume distribution, χ' can be calculated for a (large) volume distribution by postulating that at a given temperature and given measuring time, certain particles are in the superparamagnetic state and the others are in the blocked state. The susceptibility is then given by the sum of two contributions:

$$\chi'(T,\nu) = \int_{V_c}^\infty \mathrm{d}V\ Vf(V)\chi_1(T,\nu) + \int_0^{V_c} \mathrm{d}V\ Vf(V)\chi_0(T,\nu) \tag{12}$$

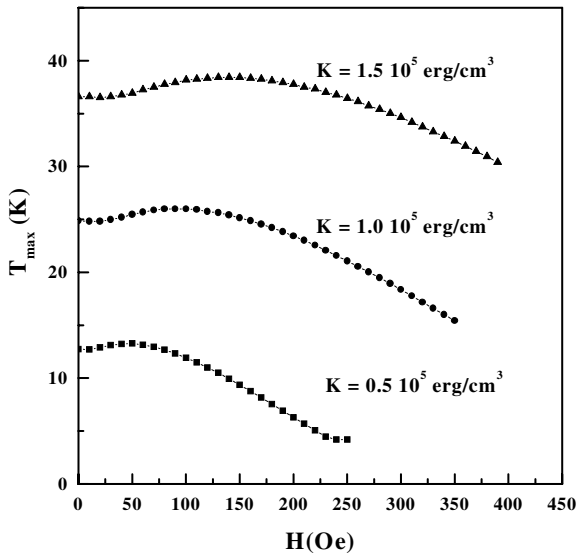
where $V_c = V_c(T, H, \nu)$ is the blocking volume defined as the volume for which $\tau = 1/\nu = \tau_m$. χ' shows a maximum at $T_{\max}$ near $\langle T_B\rangle$.

If this is done, even the simple Néel–Brown† expression for the relaxation time leads to a maximum in $T_{\max}$ when the superparamagnetic contribution to magnetization is a Langevin

† This is the simplest non-trivial case since the relaxation time (and thereby the critical volume) depends on the magnetic field.



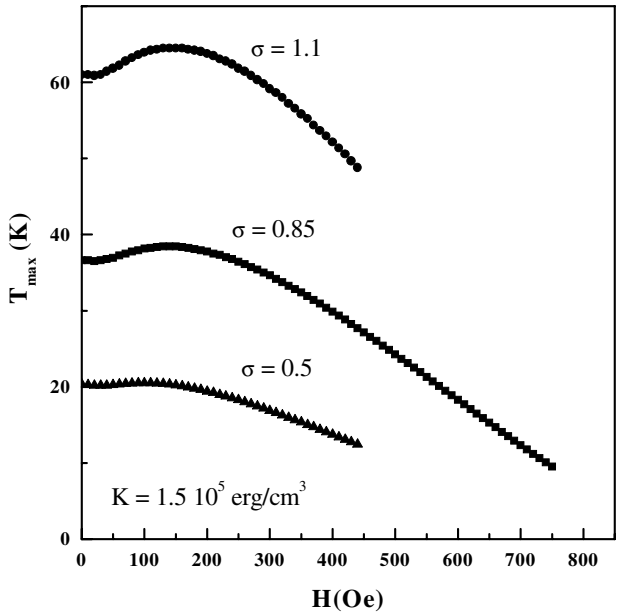
(a)



(b)

Figure 4. (a) The temperature $T_{\max}$ as a function of the applied field obtained by the calculations of section 5 and the appendix. Squares: the superparamagnetic magnetization M_{sp} is a linear function of the magnetic field given by equation (A.9). Circles: M_{sp} is the Langevin function given by equation (A.10). The parameters are the same as in figures 1–3, and $K = 1.0 \times 10^5$ erg cm^{-3}. (b) The temperature $T_{\max}(H)$ for different values of the anisotropy constant K. (c) $T_{\max}(H)$ for different values of the volume-distribution width σ, and $K = 1.5 \times 10^5$ erg cm^{-3}.

function of the magnetic field. Thus the particular expression for the single-particle relaxation time used appears not to be of crucial importance in the context of the calculation of the blocking temperature.



(c)

Figure 4. (Continued)

In figures 4(a)–4(c) we plot the results of such calculations (see the appendix), where the parameters correspond to the samples of figure 1. In figure 4(a) we compare the results for linear and non-linear (Langevin function) dependences of the magnetization on the magnetic field. We see that a non-linear dependence on H of the superparamagnetic contribution to the magnetization does indeed lead to a maximum in $T_{\max}$, while in the linear case the temperature $T_{\max}$ is a monotonic function of the field, for all values of K (corresponding to our samples). This shows that the volume distribution by itself cannot account for the non-monotonic behaviour of the temperature $T_{\max}$, contrary to what was claimed in [7].

In fact, in the non-linear case, $T_{\max}$ exhibits three different regimes with field ranges depending on all parameters and especially on K (see figures 4(a), 4(b)). For example, for $K = 1.5 \times 10^5$ erg cm^{-3}, the field ranges are (in Oe) $0.0 < H < 30, 30 < H < 140$ and $H > 140$. In the first range, i.e. for very low fields, $T_{\max}$ slightly decreases; then in the second range it starts to increase up to a maximum; and finally for very high fields $T_{\max}$ decreases down to zero. These three regimes were obtained experimentally in [7] in the case of diluted FeC particles.

Next, we studied the effect of varying the anisotropy constant K. In figure 4(b) we plot the temperature $T_{\max}$ versus H for different values of K. It is seen that, in addition to the obvious shifting of the peak of $T_{\max}$ to higher fields, this peak broadens as the anisotropy constant K increases.

We have also varied the volume-distribution width σ and the results are shown in figure 4(c). There we see that the maximum of $T_{\max}$ tends to disappear as σ becomes smaller.

Finally, these results show that the non-monotonic behaviour of $T_{\max}$ is mainly due to the non-linear dependence of the magnetization as a function of magnetic field, and that the magnetocrystalline anisotropy and the volume-distribution width have strong bearings on the variation of the curvature of $T_{\max}$ versus field.

6. Conclusions

Our attempt to explain the experimentally observed maximum in the $T_{\max}(H)$ curve for dilute samples using the asymptotic formulae for the prefactor of the relaxation rate of a single-domain particle given by Coffey *et al* [20] has led to the conclusion that these asymptotic formulae are not valid for small fields, where the maximum occurs. However, this negative result has renewed interest in the long-standing problem of finding bridging formulae for between the non-axially symmetric and axially symmetric expressions for the prefactor of the escape rate. Recently, this problem has been partially solved in [19].

On the other hand, exact numerical calculations [13, 14, 22] of the smallest eigenvalue of the Fokker–Planck matrix invariably lead to a monotonic decrease in the blocking temperature (and thereby in the temperature $T_{\max}$) as a function of the magnetic field. We may conclude then that the expression for the single-particle relaxation time does not seem to play a crucial role. Indeed, the calculations of section 5 have shown that even the simple Néel–Brown expression for the relaxation time leads to a maximum in $T_{\max}$ if one considers an assembly of particles whose magnetization, formulated through Gittleman's model, has a superparamagnetic contribution that is a Langevin function of the magnetic field. The magnetocrystalline anisotropy and the volume-distribution width have strong influences.

Another important point, whose study is beyond the scope of this work, is the effect of interparticle interactions on the maximum in the temperature $T_{\max}$. As was stated in the introduction, this maximum disappears for concentrated samples, i.e. in the case of intermediate-to-strong interparticle interactions. A recent study [25] based on Monte Carlo simulations of interacting (cobalt) fine particles seems to recover this result but does not provide a clear physical interpretation of the effect obtained. In particular, it was shown there that interactions have a strong bearing on the effective variation of the average energy barrier with field, as manifested in an increase of the curvature of the variation of $T_{\max}$ with H as the packing density (i.e. strength of interparticle interactions) increases.

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Appendix. Obtaining $T_{\max}$ from the ZFC magnetization

Here we present the (numerical) method of computing the temperature $T_{\max}$ at the peak of the zero-field-cooled magnetization for non-interacting nanoparticles.

The potential energy for a particle reads

$$\frac{\beta U}{\alpha} = \sin^2\theta - 2h\cos(\psi - \theta) \tag{A.1}$$

where all parameters are defined in section 3.

Then, one determines the extrema of the potential U and defines the escape rate λ according to the symmetry of the problem. Here we consider, for simplicity, the axially symmetric Néel–Brown model where λ is given by equation (5).

The next step consists in finding the critical volume V_c introduced in equation (12). V_c is defined as the volume at which the relaxation time (or the escape rate) is equal to the measuring

time $\tau_m = 100$ s (or measuring frequency). That is, if one defines the function

$$F(V) = \lambda(\alpha, \theta_a, \theta_m, \theta_b) - \frac{\tau_N}{\tau_m} \tag{A.2}$$

where θ_a, θ_b, θ_m correspond to the two minima and the maximum of the potential, respectively, the critical volume V_c is obtained as the volume that nullifies the function $F(V)$ for given values of T, H and all other fixed parameters (γ, η_r, M_s and the volume-distribution width σ).

Then, M_{zfc} is defined according to Gittleman's model [6]; that is,

$$ZM_{zfc}(H, T, \psi) = \int_0^{V_c} \mathcal{D}V\ M_{sp}(H, T, V, \psi) + \int_{V_c}^{\infty} \mathcal{D}V\ M_b(H, T, V, \psi) \tag{A.3}$$

where M_{sp} and M_b are the contributions to the magnetization from superparamagnetic particles with volume $V \leqslant V_c$ and particles still in the blocked state with volume $V > V_c$.

$$f(V) = (1/\sigma\sqrt{2\pi}) \exp(-\log^2(V/V_m)/2\sigma^2)$$

is the log–normal volume distribution, V_m being the mean volume;

$$Z \equiv \int_0^{\infty} \mathcal{D}V = \int_0^{\infty} Vf(V)\, \mathrm{d}V.$$

Equation (A.3) can be rewritten as

$$ZM_{zfc} = \int_0^{V_c} \mathcal{D}V\ M_{sp} - \int_0^{V_c} \mathcal{D}V\ M_b + \int_0^{\infty} \mathcal{D}V\ M_b. \tag{A.4}$$

Now, using

$$M_b(H, T, V, \psi) = \frac{M_s^2 H}{2K} \sin^2 \psi \tag{A.5}$$

M_b can be taken outside the integral in the last term above. Thus†,

$$ZM_{zfc} = \int_0^{V_c} \mathcal{D}V\ (M_{sp} - M_b) + ZM_b.$$

The final expression of M_{zfc} is obtained by averaging over the angle ψ ($\langle \sin^2 \psi \rangle = \frac{2}{3}$):

$$M_{zfc} = \frac{1}{Z} \int_0^{\pi/2} \mathrm{d}\psi\ \sin\psi \int_0^{V_c} \mathcal{D}V\ (M_{sp} - M_b) + \frac{M_s^2 H}{3K}. \tag{A.6}$$

The expression of M_{sp} varies according to the model used. Chantrell *et al* [26] have given an expression which is valid for $M_s HV/k_B T \ll 1$:

$$M_{sp}(H, T, V, \psi) = \frac{M_s^2 VH}{k_B T} \left(\cos^2 \psi + \frac{1}{2} \left[1 - \cos^2 \psi \left(1 - \frac{I_2}{I_0} \right) \right] \right) \tag{A.7}$$

with

$$\frac{I_2}{I_0} = \frac{1}{\alpha} \left(-\frac{1}{2} + \frac{\mathrm{e}^{\alpha}}{I(\alpha)} \right) \qquad I(\alpha) = 2 \int_0^1 \mathrm{d}x\ \mathrm{e}^{\alpha x^2}. \tag{A.8}$$

Note that upon averaging over ψ, the expression in (A.7) reduces to

$$M_{sp}(H, T, V) = \frac{M_s^2 VH}{3k_B T} \tag{A.9}$$

which is just the limit of the Langevin function for $M_s HV \ll k_B T$, i.e.

$$M_{sp}(H, T, V) = M_s \mathcal{L}\left(\frac{M_s HV}{k_B T} \right). \tag{A.10}$$

† The reason for doing this is to avoid computing the integral $\int_{V_c}^{\infty}$ which is numerically inconvenient.

Therefore, the expression in (A.6) becomes

$$M_{zfc} = \frac{1}{Z}\int_0^{V_c} \mathcal{D}V\ (M_{sp} - M_b) + \frac{M_s^2 H}{3K} \tag{A.11}$$

This is valid only in the case of a relaxation time independent of ψ, as in the Néel–Brown model, which is applicable to an assembly of uniformly oriented particles. However, if one wanted to use the expressions for the relaxation time given by Coffey *et al* and others, where τ depends on the angle ψ, as is the case in reality, one should not interchange integrations over ψ and V, as is done in (A.6), since V_c in general depends on τ and thereby on ψ.

Therefore, the final expression for M_{zfc} that was used in our calculations for determining the temperature $T_{\max}$ is given by equations (A.9), (A.10), (A.11).

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